

CHAPTER 3
EPA/NSF ETV
EQUIPMENT VERIFICATION TESTING PLAN FOR SOC OXIDATION BY OZONE
AND ADVANCED OXIDATION PROCESSES

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1.0 APPLICATION OF THIS VERIFICATION TESTING PLAN

This document is the ETV Testing Plan for evaluation of water treatment equipment utilizing ozone for oxidation of man-made or synthetic organic chemicals (SOCs). This Testing Plan is to be used as a guide in the development of the Product-Specific Test Plan (PSTP) for testing ozone equipment, within the structure provided by the "EPA/NSF ETV Protocol For Equipment Verification Testing For The Removal Of Synthetic Organic Chemical Contaminants: Requirements For All Studies." This ETV plan is applicable only to treatment systems that rely on ozone to oxidize SOCs in water. Systems using ozone oxidation for reasons other than SOC oxidation (i.e., taste and odor control, disinfection) are not required to conduct the experiments outlined in this ETV plan. Systems may incorporate unique strategies for enhancing the effect of ozone on SOC concentrations, such as the use of ozone/advanced oxidation processes (ozone/AOPs) combining ozone with ultraviolet (UV) light or hydrogen peroxide. All ozone technologies, including ozone/AOPs, may be tested under this plan.

In order to participate in the equipment verification process for SOC oxidation by ozone or ozone/AOPs, the equipment Manufacturer and the designated Field Testing Organization shall use the procedures and methods described in this test plan, and in the "EPA/NSF ETV Protocol For Equipment Verification Testing For The Removal Of Synthetic Organic Chemical Contaminants: Requirements For All Studies" as guidelines for development of the PSTP.

This ETV test plan is applicable to the testing of water treatment equipment utilizing ozone or ozone/AOPs for SOC oxidation in drinking water. This plan is applicable to both surface water and groundwater supplies.

2.0 INTRODUCTION

The organic compounds present in source waters are characterized as either: 1) naturally occurring (e.g., humic acid, fulvic acid); or 2) synthetic (e.g., pesticides, hydrocarbons, phenols, dyes, amines, solvents, and plasticizers, etc.).

Ozone is a powerful oxidant that is applied during water treatment for microbial inactivation as well as oxidation of organic compounds, metals, and taste and odor causing compounds. The use of ozone in potable water treatment in the United States has increased substantially in the last 20 years, due to its superior inactivation of microorganisms (i.e., cysts) relative to chlorine, chloramine, and chlorine dioxide and its ability to reduce the concentrations of certain organics in drinking water.

Ozone is applied to drinking water as a gas, which is generated on-site. The ozone gas is transferred into a dissolved state by either bubbling or injecting ozone gas into the process stream. Ozone can be applied to untreated (raw) or treated (e.g., coagulated/settled or filtered) water. In this ETV plan, the oxidation of SOCs by ozone or ozone/AOPs will be evaluated. Ozone/AOPs, which typically combine ozonation with UV light or hydrogen peroxide, convert dissolved ozone to hydroxyl radicals. In many instances, ozone/AOPs can be more effective than ozone used by itself for oxidation of SOCs.

3.0 GENERAL APPROACH

Testing of equipment covered by this ETV plan will be performed by an NSF-qualified Field Testing Organization (FTO) that is selected by the equipment Manufacturer. Water quality analytical work to be carried out as part of this ETV plan will be contracted with a state-certified or third party- or EPA-accredited qualified analytical laboratory.

4.0 OVERVIEW OF TASKS

4.1 Initial Operations: Overview

The purpose of these tasks is to provide preliminary information which will facilitate final test design and data interpretation.

4.1.1 Task A: Characterization of Feed Water

The objective of this Initial Operations task is to obtain a chemical and physical characterization of the feed water for those systems using ozone or ozone/AOPs for SOC oxidation. Historical records of SOC concentrations in the feed water shall be reviewed to evaluate the use of ozone or ozone/AOPs at the site.

A thorough description of the watershed or aquifer and any pretreatment modules that provide the feed water should be prepared, to aid in interpretation of feed water characterization.

4.1.2 Task B: Initial Test Runs

During Initial Operations, the manufacturer may want to evaluate equipment operation and determine flow rates, hydraulic retention time, ozone dosage, optimum pH, sequencing or timing of UV light and/or hydrogen peroxide addition relative to ozonation, or other factors which provide effective treatment of feed water. This is a recommended Initial Operations task.

The FTO may also want to work with the analytical laboratory to perform blank or preliminary challenges and sampling routines to verify that sampling equipment can perform its required functions. This is also a recommended Initial Operations Task.

4.2 Verification Operations: Overview

The objective of this task is to operate for a minimum of one test period the treatment equipment provided by the FTO and to assess its ability to meet stated water quality goals and any other performance objectives specified by the Manufacturer. The equipment shall be operated to collect data on equipment performance and water quality for purposes of performance verification. The test period selected should represent the worst-case for concentrations of ozone demanding contaminants (e.g.,

iron, organics, hydrogen sulfide, pesticides, or turbidity) and for presence of synthetic organic contaminants.

4.2.1 Task 1: Verification Testing Runs and Routine Equipment Operation

To characterize the technology in terms of efficiency and reliability, water treatment equipment that includes ozone (or ozone/AOPs) shall be operated for Verification Testing purposes with the operational parameters based on the results of the Initial Operations testing.

4.2.2 Task 2: Feed Water and Finished Water Quality

During each Verification Testing period, feed water and treated water samples shall be collected and analyzed for those parameters relevant to oxidation performance and affecting equipment performance, as outlined in Section 10, Table 1.

4.2.3 Task 3: Documentation of Operating Conditions and Treatment Equipment Performance

During each Verification Testing period, operating conditions and performance of water treatment equipment shall be documented. This includes ozone feed gas concentration, gas and liquid pressures, gas and liquid temperatures, gas and liquid flow rates, ozone off-gas concentration, applied and transferred ozone dosage, power usage for the ozone generator, ozone transfer equipment, ozone feed-gas and off-gas monitors (if part of the ozone system) and ozone destruct unit, as well as stability of the electrical power supply (surges, brown-outs, etc.).

If ozone (or an AOP) is used following pretreatment (e.g., coagulation/settling), then a complete description of the pretreatment process shall be provided. For AOP systems, the operating conditions and parameters associated with hydrogen peroxide or UV light equipment must also be documented.

4.2.4 Task 4: SOC Oxidation

The objective of this task is to evaluate SOC oxidation during Verification Testing by measuring the SOC concentrations of interest in the feed water and in the treated water. If the SOC concentration naturally present in the feed water is not sufficiently high for testing, SOC spiking is needed. Another requirement of this task is to provide a gas chromatography/mass spectrometry scan of the organic by-products formed by ozonation of SOC.

4.2.5 Task 5: Data Management

The objective of this task is to establish an effective field protocol for data management at the field operations site and for data transmission between the FTO and the NSF for data obtained during the Verification Testing. Prior to the beginning of field testing, the database design must

be developed by the FTO and reviewed and approved by NSF. This will ensure that the required data will be collected during the testing, and that it can be effectively transmitted to NSF for review.

4.2.6 Task 6: Quality Assurance/Quality Control (QA/QC)

An important aspect of Verification Testing is the protocol developed for quality assurance and quality control. The objective of this task is to assure accurate measurement of operating and water quality parameters during ozone equipment Verification Testing. Prior to the beginning of field testing, a QA/QC plan must be developed which addresses all aspects of the testing process. Each water quality parameter and operational parameter must have appropriate QA and QC measures in place and documented. For example, the protocol for ozone measurement using a spectrophotometer should describe how the instrument is calibrated, what adjustments are made, and provide a permanent record of all calibrations and maintenance for that instrument.

5.0 TESTING PERIODS

The required tasks in the Verification Testing Plan (Tasks 1 through 6) are designed to be carried out during one or more testing periods, each of which shall provide at least 200 hours of ozone equipment operation. During this time, the performance and reliability of the equipment shall be documented.

Some systems may operate for less than 24 hours per day. Interruptions in ozone production are allowed but the reason for and duration of all interruptions shall be fully described in the Verification Testing report. Any testing conducted at intervals of less than 200 hours is considered a test *run*, whereas the entire 200 hours (either continuous or as the sum of individual test runs) of ozone equipment operation is considered the Verification Test *period*. If ozone production is interrupted during a verification test run, that test run shall be considered to have been concluded at the time of interruption of the ozone feed. After restart, all data collected are to be part of a new verification test run.

6.0 DEFINITION OF OPERATIONAL PARAMETERS

Definitions that apply to ozone and ozone/AOP processes are given below. Refer to Appendix A of *Ozone in Water Treatment, Application and Engineering*, by the American Water Works Association Research Foundation and Compagnie Générale des Eaux, Lewis Publishers, 1991 for a more detailed description of terms.

6.1 Feed Gas or Ozone Production Concentration (% weight or g/m³ NTP)

The feed gas or ozone production concentration (Y_1) is the ozone concentration (in gaseous form) being applied to the water being treated. It is expressed in units of g/m³ normal temperature and pressure

(NTP) or as percent by weight. The temperature and pressure values associated with NTP are 0 °C and one atmosphere (i.e., 14.696 psi, 760 mm Hg, or 101.325 kPa), respectively.

6.2 Off Gas Concentration (% weight or g/m³ NTP)

The off gas concentration (Y_2) is the ozone concentration (in gaseous form) of the gas which is being released (i.e., off gas) from the water being treated. This off gas contains ozone which was not transferred into a dissolved form during treatment. It is expressed in units of g/m³ NTP or as percent by weight.

6.3 Applied Ozone Dosage (mg/L)

The amount of ozone added to the water being treated is the applied ozone dosage. The equation for calculating the applied ozone dosage is as follows:

$$D = P/(8.34*L)$$

where: D = applied ozone dosage (mg/L)
P = ozone production (lb/day)
L = water flow rate (MGD, million U.S. gallons per day)

6.4 Transfer Efficiency (percent)

The transfer efficiency is defined as the percentage of ozone that becomes dissolved into the water being treated. The equation for calculating the transfer efficiency is as follows:

$$TE = [(Y_1 - Y_2)/Y_1]*100$$

where: TE = transfer efficiency (percent)
 Y_1 = ozone production concentration (g/m³ NTP or percent by weight)
 Y_2 = off gas ozone concentration (g/m³ NTP or percent by weight)

This calculation assumes that the flow of the feed gas is equal to the flow of the off gas. The transfer efficiency calculation can be refined by measuring both gas flow rates or by monitoring the dissolved gas concentration in the liquid phase if the Manufacturer and their FTO desire.

6.5 Transferred Ozone Dosage (mg/L)

The transferred ozone dosage is the concentration of ozone that becomes dissolved into the water being treated. The equation for calculating the transferred ozone dosage is as follows:

$$T = (D * TE)/100$$

where: T = transferred ozone dosage (mg/L)

D = applied ozone dosage (mg/L)
TE = transfer efficiency (percent, i.e., 95.0 and not 0.95)

6.6 Dissolved Ozone Concentration (mg/L)

The concentration of ozone in solution is the dissolved ozone concentration. It is measured using an indigo bleaching technique (e.g., HACH AccuVac or *Standard Method* 4500-O₃ B) or by inserting a dissolved ozone probe into the process stream (e.g. Orbisphere, Orbisphere Laboratories, Emerson, NJ).

6.7 Ozone Decay Rate (1/min)

After the initial ozone demand has been satisfied, the ozone decay rate is assumed to follow pseudo first-order kinetics. Monitoring the decay rate will provide an indication of the level of ozone demanding substances present in the feed water and the environmental conditions affecting oxidation (e.g., pH and temperature). To calculate the decay rate, the initial ozone concentration (C_o) at time zero and the ozone concentration (C) after time, t, must be known. The equation for calculating the decay rate (k) is as follows:

$$C = C_o e^{-kt}$$

where: C = ozone concentration at time t (mg/L)
C_o = ozone concentration at time zero (mg/L)
t = contact time (minutes)
k = decay coefficient (1/minute)

If possible, the ozone residual should be measured after several contact times in the reactor. The best fit line of ln(C/C_o) versus t can be used to obtain the decay coefficient, k. If the plot does not fit a straight line, the assumption of pseudo-first order kinetics is not valid.

7.0 TASK A: CHARACTERIZATION OF FEED WATER

7.1 Introduction

This recommended Initial Operations task is performed to determine if the chemical, biological, and physical characteristics of the feed water are appropriate for the water treatment equipment to be tested.

Initial Operations (Tasks A and B) are not mandatory but they are recommended as an aid to successful completion of Verification Testing. If the verification entity conducts a site visit for QA purposes, then Task B would need to be performed.

7.2 Objectives

The objective of this task is to obtain a complete chemical and physical characterization of the source water, or the feed water after pre-treatment, that will be entering the treatment system being tested.

7.3 Work Plan

During this Initial Operations task, the following water quality characteristics of the feed water to the ozone system should be measured and recorded for both ground and surface waters: ozone demand, turbidity, temperature, pH, alkalinity, calcium, total hardness, total sulfides, total organic carbon, dissolved organic carbon, ultraviolet absorbance (at 254 nm), color, bromide, iron, and manganese. Data on SOC's in the feed water (source water) should be obtained from existing databases or by analysis of water samples, so a determination about the need for SOC spiking can be made.

Sufficient information shall be obtained to illustrate the variations expected to occur in these parameters that will be measured during the Verification Testing for a typical annual cycle for the water source. This information will be compiled and shared with NSF so NSF and the FTO can determine the adequacy of the data for use as the basis to make decisions on the testing schedule.

A brief description of the watershed or aquifer source shall be provided, to aid in interpretation of feed water characterization. The watershed description should include a statement of the approximate size of the watershed, a description of the topography (i.e., flat, gently rolling, hilly, mountainous) and a description of the kinds of human activity that take place (i.e., mining, manufacturing, cities or towns, farming, wastewater treatment plants) with special attention to potential sources of pollution that might influence feed water quality. The nature of the water source, such as stream, river, lake or man-made reservoir, should be described as well. Aquifer description should include (if available) the above characterization relative to the recharge zone, a description of the hydrogeology of the water bearing stratum(a), well boring data, and any Microscopic Particulate Analysis data indicating whether the groundwater is under the influence of surface waters.

Any pretreatment, including oxidation, coagulation or pH adjustment, of the water upstream of the ozone equipment shall be completely documented and characterized. Any coagulant or other chemical additions shall be identified and the chemical form and dosage shall be fully described.

7.4 Analytical Schedule

There is no recommended analytical schedule for characterization of the feed water. Any existing water quality data should be reviewed to assess the character of the feed or source water as well as the range of water quality that can be expected during each season. Water quality sampling can be performed if there are data gaps in the existing information.

7.5 Evaluation Criteria

Feed water quality will be evaluated in the context of the Manufacturer's statement of the equipment performance objectives but should not be beyond the range of water quality suitable for treatment for the equipment in question. The device shall be tested using water of the quality for which the equipment was designed.

8.0 TASK B: INITIAL TEST RUNS

8.1 Introduction

During the Initial Operations, a Manufacturer and their FTO may choose to evaluate equipment operations and determine flow rates, hydraulic residence time, ozone production, power supply requirements, or other factors applicable to the technology and related to effective treatment of the feed water, including the weight ratios of hydrogen peroxide to ozone dosages and/or the ratios of UV to ozone dosages. The Manufacturer may also choose to work with the FTO and the analytical laboratory to perform blank or preliminary challenges (if necessary) and sampling routines to verify that sampling equipment can perform the required functions under normal operating conditions. This information may also indicate operating conditions under which the Manufacturer's stated performance objectives are not met. This is a recommended Initial Operations task. An NSF field inspection of equipment operations and sampling and field analysis procedures may be carried out during the initial test runs, and if this occurs, the Initial Operations task must be performed.

8.2 Objectives

The objective of these test runs is to bracket the proper operating parameters for treatment of feed water during Verification Testing. The ability of ozone or ozone/AOP systems to effectively oxidize SOC's and reduce their concentrations will vary depending on the quality of the feed water being treated and the season. Therefore, conducting initial test runs is strongly recommended.

8.3 Work Plan

Because Initial Operations test runs are not a requirement of this ETV plan, the Manufacturer and FTO can decide the duration of Initial Operations. Enough time should be available to establish optimal operating conditions and to ensure that the system will be able to meet any performance objectives.

8.4 Analytical Schedule

Because these Initial Operations are being conducted to define future operating conditions for Verification Testing, a strictly defined schedule for sampling and analysis does not need to be followed. Adhering to the schedule for sampling and analysis to be followed during Verification Testing is recommended, however, so the operator can gain familiarity with the time requirements that will be applicable during Verification Testing. Also, during the Initial Operations phase, the verification

organization may conduct an initial on-site inspection of field operations, sampling activities, and on-site analyses. The sampling and analysis schedule that is to be used during Verification Testing shall be followed during the on-site inspection.

8.5 Evaluation Criteria

The Manufacturer and the FTO should evaluate the data produced during the Initial Operations to determine if the water treatment equipment performed in a manner that will meet or exceed the statement of performance objectives. If performance is not as good as in the statement of performance objectives, the FTO may conduct additional Initial Operations or cancel the remainder of the testing program.

9.0 TASK 1: VERIFICATION TESTING RUNS AND ROUTINE EQUIPMENT OPERATION

9.1 Introduction

Water treatment equipment that includes ozone or ozone/AOPs shall be operated for Verification Testing purposes with operational parameters based on the manufacturer's statement of performance objectives.

9.2 Experimental Objectives

The objective of this task is to operate the ozone or ozone/AOP equipment and characterize the effectiveness and reliability of the equipment.

9.3 Work Plan

9.3.1 Verification Testing Runs

The Verification Testing Runs in this task consist of an evaluation of the treatment system, using the most successful treatment parameters defined during Initial Operations. Performance and reliability of the equipment shall be tested during one or more Verification Testing periods consisting of at least 200 hours of ozone production at the test site.

Verification Testing should be conducted at times when worst-case seasonal water quality conditions exist, including peak concentrations of SOC_s or of hydroxyl free radical-demanding contaminants or ozone-demanding contaminants. During each of these testing periods, Tasks 1 through 6 shall be conducted simultaneously.

Factors that can influence SOC oxidation include:

- the presence of ozone demanding substances that may be present in the form of particulate matter, dissolved organic matter, or dissolved inorganic matter; often occurring in the spring, or during reservoir or lake turn-over events, or also encountered in rivers carrying a high sediment load or in surface waters during periods of high runoff resulting from heavy rains or snow melt. Algae also exert an ozone demand as do iron, manganese, and cyanide. The presence of ozone demanding substances will affect the ability of ozone to effectively oxidize SOC_s and will react with hydroxyl free radicals needed to destroy the slower-to-oxidize SOC_s.
- pH and alkalinity, which can vary seasonally, will affect the decay rate of ozone in natural waters, and may affect the amount of SOC oxidation achieved by the system.
- temperature.

9.3.2 Routine Equipment Operation

If the water treatment equipment is being used for production of potable water during the time intervals between verification runs, routine operation of the equipment will occur. In this situation, the operating and water quality data collected and furnished to the Safe Drinking Water Act (SDWA) primacy agency shall be supplied to the NSF-qualified FTO for use in evaluating conditions during verification testing.

For equipment that is being used to treat water for distribution to customers, it is assumed that the State has already issued a permit (if one is necessary) for installation and operation. If ETV is being conducted to establish the SOC oxidation capabilities of the existing equipment, permission by the State may be required if the system were taken off-line for verification testing.

9.4 Schedule

During Verification Testing, water treatment equipment shall be operated for a minimum of 200 hours. The reason for and duration of any interruptions in ozone production during Verification Testing shall be fully documented.

9.5 Evaluation Criteria

The goal of this task is to operate the equipment for 200 hours during Verification Testing. Data shall be provided to substantiate that 200 hours of operation have been completed.

10.0 TASK 2: FEED WATER AND TREATED WATER QUALITY

10.1 Introduction

Water quality data shall be collected during Verification Testing for the feed water and treated water as shown in Table 1. The Field Test Organization, on behalf of the equipment Manufacturer, shall assure the sampling or measuring of the water quality parameters in Table 1. The FTO may use local personnel to assist in collection of samples or measurement of test parameters, but is responsible for their training to assure proper techniques are used at all times.

10.2 Experimental Objectives

The objective of this task is to identify the presence and concentration of water quality characteristics that might affect the ability of ozone to oxidize SOC. This task will also provide data to ensure that the use of ozone does not increase the risk of violating any existing or future SDWA regulations (e.g., THMs, bromate).

10.3 Work Plan

The Manufacturer or FTO will be responsible for establishing the testing operating parameters, on the basis of the Initial Operations testing. Many of the water quality parameters described in this task will be measured on-site by the NSF-qualified FTO or by local community personnel properly trained by the FTO. Analysis of the remaining water quality parameters will be performed by a state-certified or third party- or EPA-accredited analytical laboratory. The methods to be used for measurements of water quality parameters in the field are listed in the Analytical Methods section in Table 2. The analytical methods utilized in this study for on-site monitoring of feed water and treated water qualities are described in Task 6, Quality Assurance/Quality Control (QA/QC). Where appropriate, the *Standard Methods* reference numbers for water quality parameters are provided for both the field and laboratory analytical procedures. EPA Methods for analysis of the parameters listed in Table 2 also may be used.

Samples of the feed water shall be collected and analyzed for background SOC concentrations. Feed water shall also be sent to the state-certified or third party- or EPA- accredited laboratory to conduct spiking QA/QC analysis (see Task 6). The approved analytical methods for SOC vary, depending on the SOC(s) of interest. A state-certified or third party- or EPA-accredited laboratory should be using an approved EPA or *Standard Method* for SOC analysis. Peer-reviewed and proposed methods for SOC determination are also allowable if approved EPA or *Standard Methods* are not available. The preservatives needed for sample collection also vary for different SOC(s) and the state-certified or third party- or EPA-accredited should fully document sampling requirements for the FTO.

Any disinfectant added upstream of the ozone addition point will affect the ozone demand; therefore, an agreement between NSF, the manufacturer, and the FTO must be made to determine whether or not to allow pre-disinfection prior to ozonation during the Verification Testing Period. If a pre-disinfectant is used, testing shall be conducted to verify that no disinfectant residual exists at the influent of the ozone

contactor, or if a disinfectant residual does exist, a quenching solution (e.g., sodium bisulfite or hydrogen peroxide) shall be used. The latter option (quenching) is less desirable because the concentration of the quenching agent will have to be carefully monitored during testing to minimize over-feeding of the quenching agent (which would result in an ozone demand).

10.4 Analytical Schedule

Water quality data shall be collected at the intervals specified in Table 1. Additional sampling and data collection may be performed at the discretion of the Manufacturer and their designated FTO. Sample collection protocol shall be defined by the FTO in the PSTP. Algae sampling is not required for systems using groundwater sources.

For water quality samples that will be shipped to a state-certified or third party- or EPA-accredited laboratory for analysis, the samples shall be collected in appropriate containers (containing preservatives as needed) prepared by the laboratory. These samples shall be preserved, stored, shipped, and analyzed in accordance with appropriate procedures and holding times, as specified by the laboratory. Original field sheets and chain-of-custody forms shall accompany all samples shipped to the laboratory. Copies of field sheets and chain-of custody forms for all samples shall be provided to NSF.

10.5 Evaluation Criteria

The performance of the ozone or ozone/AOP equipment will be compared to the Manufacturer's statement of performance objectives for the equipment being tested.

11.0 TASK 3: DOCUMENTATION OF OPERATING CONDITIONS AND TREATMENT EQUIPMENT PERFORMANCE

11.1 Introduction

Throughout the Verification Testing period, operating conditions shall be documented. This shall include descriptions of pretreatment chemistry and filtration performance for the equipment processes, if used, and their operating conditions. The performance of the ozone equipment (including ozone generator(s), air preparation system(s), off-gas destruct unit(s), injection equipment, ozone monitor(s), and contactor(s)) as well as UV light and hydrogen peroxide equipment shall be documented. The total volume of water treated and the total power usage for all equipment associated with the ozone or ozone/AOP system shall also be recorded.

11.2 Objectives

The objective of this task is to accurately and fully document the operating conditions during treatment, and the performance of the equipment. This task is intended to collect data that describe operation of the equipment and information that can be used to develop cost estimates for operation of the equipment.

11.3 Work Plan

During Verification Testing, treatment equipment operating parameters for both pretreatment and ozonation shall be monitored and recorded on a routine basis by the NSF-qualified FTO or by local community personnel properly trained by the FTO.

Table 3 outlines some of the operating parameters that shall be monitored throughout Verification Testing. Operating parameters, in addition to those listed in Table 3, may be needed to adequately assess the operating conditions of the ozone or ozone/AOP equipment. These additional parameters shall be identified by the Manufacturer and the FTO and agreed upon by the Manufacturer and NSF.

Examples of operational parameters which shall be monitored are:

- water flow rates
- gas flow rates
- water pressures
- gas pressures
- water temperatures
- gas temperatures
- ozone operating voltage
- ozone production power consumption
- air preparation power consumption or other consumables for air preparation
- oxygen feed rate (if applicable) and other pertinent operation information
- performance of oxygen generation or oxygen feed equipment
- ozone electrical frequency, if variable
- amperage of ozone equipment
- weight ratio of hydrogen peroxide (if used) to ozone

On a daily basis, the operator shall note and record whether any visual effects of ozonation are apparent in the treated water or on piping or vessels that convey or hold treated water. This may include surface scum, precipitation of metals, color changes, etc. At the end of the test period if an ozone contact chamber is provided with the equipment and if it is accessible, the contact chamber shall be inspected for deposits of scum, precipitation of metals, or color changes, and this information shall be noted in the Verification Testing report.

11.4 Schedule

Table 3 presents the schedule and recording data required for ozone and AOP systems. The length of time (hours) of operation (during Verification Testing) shall be recorded for all of the ozone and AOP equipment.

11.5 Evaluation Criteria

Where applicable, the data developed from this task will be compared to statements of performance objectives. If no relevant statement of performance capability exists, results of operating and performance data will be tabulated for inclusion in the Verification Report.

12.0 TASK 4: DOCUMENTATION OF EQUIPMENT PERFORMANCE: SOC OXIDATION

12.1 Introduction

The ability of ozone and AOP equipment to oxidize SOC(s) can be assessed by measuring the initial and final SOC concentrations and computing the change (see Chapter 1 of the Protocol for Equipment Verification Testing of Synthetic Organic Contamination Removal).

12.2 Experimental Objectives

The objective of this task is to determine the effectiveness of ozone or ozone/AOP equipment for SOC oxidation at small systems.

12.3 Work Plan

The FTO shall conduct water quality sampling and calculate the reduction in SOC concentration(s) resulting from ozone or AOP treatment. Task 4 shall be conducted during the Verification Testing runs conducted in Task 1, 2, and 3.

The background or naturally occurring concentration of the SOC(s) of interest shall be determined during either Task A or Task 2 so that the background concentration of SOC(s) in the feed water is known prior to conducting Verification Testing. If the background SOC concentration is too low to adequately show or calculate a percentage removal, spiking of SOC(s) during the 200 hours of Verification Testing will be necessary.

Multiple SOC(s) can be simultaneously evaluated during Verification Testing; however, ozone or AOPs may preferentially react with naturally occurring organics or other SOC(s) present in solution, thereby reducing its ability to oxidize the SOC(s) of interest. Thus, it is possible that the desired outcome of Verification Testing may not occur during some multiple SOC evaluations.

If the ozone or AOP equipment is already being used at a site and has been approved by the State (if necessary), a manufacturer may want to verify its performance with Verification Testing. This can be accomplished by conducting the tests at the location if naturally occurring or background SOC concentrations are high enough for accurately and precisely calculating reductions. This would not compromise the water quality in any way. However, if SOC(s) must be spiked for testing, this poses a potential threat to the water quality. In this case, identical equipment would have to be brought on site

and spiked SOC studies would have to be conducted with this additional equipment. The effluent of this spiked SOC testing would be treated as described in Section 12.3.5.

12.3.1 Types of SOC's

This ETV plan is not designed to guide Verification Testing for volatile organic compounds (VOCs). Examples of VOCs include benzene and vinyl chloride, and a list of regulated VOCs (i.e., Phase I) can be found in Pontius (1998).

Oxidation of SOC's by ozone or AOPs can form by-products. The presence and concentration of these by-products is of interest because some of the by-products are considered as potential health concerns as a result of long-term exposure. Therefore, it is necessary that one treated water sample be collected during each Verification Test period, and this sample will be analyzed for the presence and concentration of by-products. This can be accomplished by conducting a scan of semi-volatile organic by-products by using gas chromatography/mass spectrometry by a state-certified or third party- or EPA-accredited analytical laboratory that has scanning and compound library matching capabilities. Some of the common by-products include: aldehydes, ketones, and for atrazine, deethylatrazine and deisopropylatrazine.

12.3.2 Spiking Protocols

Spiking of SOC's shall be used in concentrations sufficient to permit the highest level of stress for the Manufacturer's equipment. Some guidelines for spiking include:

- SOC spiking shall begin at start-up of the treatment equipment and shall continue for the 200 hours of Verification Testing.
- The SOC(s) feed solution shall be prepared by diluting the SOC into dilution water that is distilled or deionized and oxidant demand-free.
- The container used for storing the feed SOC solutions shall be chemically inert (i.e., not reactive or adsorbable with the SOC(s) of interest).
- The feed solution shall be gently and continuously mixed throughout the Verification Test Run.
- The SOC spiked solution shall be fed using an adjustable rate chemical feed pump.
- Use of an in-line static mixer to mix this solution into the feedwater is recommended.
- SOC samples shall be collected in sample bottles prepared (i.e., preservatives added, if necessary) by the analytical laboratory performing the analysis.
- Multiple SOC's can be contained in the same stock feed container (i.e., having only one feed solution).
- The concentration of SOC(s) applied to the feed water shall be agreed upon by the Manufacturer, NSF, and the FTO.

12.3.3 Test Operation and Sample Collection

If spiking is necessary, the SOC(s) of interest shall be continuously applied to the feed water during the 200 hours of Verification Testing. If an ozone or ozone/AOP system is temporarily shut down, then the spiking solution feed equipment should also be shut down and then started again when the ozone or ozone/AOP system is started again.

During the Verification Testing period, SOC samples of the feed water and treated water shall be collected once per 25 hours of operation. If the ozone or ozone/AOP system is not operating continuously, then the SOC samples shall be collected after the mid-point of the run in which the equipment is being operated. For example, if the ozone system is operated in 8 hour shifts, the SOC samples shall be collected after the fourth hour of operation.

During sample collection, minimal sample agitation and exposure to the atmosphere shall occur. An overflowing technique for filling samples bottles is recommended. A piece of Tygon tubing attached to the sample port can be placed such that the unattached end of the tubing rests at the bottom of the sampling container. As the sample fills the bottle, the end of the tubing remains at the bottom of the container. Once the sampling container is overflowing, the tubing can slowly be removed from the container. The lid should be placed on the container immediately after the sample tube is removed from the sample container.

Since some SOC samples require the use of a preservative in the sampling container, the overflowing technique is not applicable to all SOC(s). If this is the case, the Tygon tubing is still recommended (to minimize sample agitation during collection); however, the tubing should be removed prior to the point at which the sample would overflow the container.

Samples shall be delivered to a state-certified or third party- or EPA-accredited analytical laboratory for analysis using approved EPA or *Standard Methods* for measuring the SOC concentrations of interest.

12.3.4 Experimental Quality Control

Duplicates of the feed and treated water samples shall be collected for at least two of the sampling events during a Verification Test Run. A process control and trip control sample shall also be collected as part of Task 6.

The experimental quality control shall be verified by checking the flow rate of the spiked solution once per day. To ensure the proper feed rate of the spiked SOC solution to the ozone or AOP system, use a stopwatch to measure the time required to collect a specified volume of the feed solution from the feed system. This requires that the feed line to the contactor be temporarily disconnected so that the pumping rate of the stock SOC solution can be measured. Typically, a graduated cylinder is used to collect the pumped SOC sample and the size of the graduated cylinder is such that the length of collection time exceeds 10 seconds.

12.3.5 Treatment of Effluent

Treated water resulting from SOC spiking experiments using ozone or ozone/AOP equipment shall not be distributed to the public. The treated water might have to be passed through a granular activated carbon (GAC) filter for removal of residual SOC's during the 200 hours of Verification testing. The size of the GAC filter and the type of carbon would need to be determined by the Manufacturer and FTO and approved by the State's pollution control authority. Since some SOC's are more readily adsorbed than others, and there may be competition between SOC's for adsorption sites on the carbon, GAC filters would have to be designed on a case-by-case basis. The discharge of treated water shall be directed to a location that is approved by the State.

12.4 Analytical Schedule

Feed water and treated water SOC samples shall be collected once per 25 hours of operation. Duplicate sampling is required for two of the samples of Verification Testing.

12.5 Evaluation Criteria

The difference in concentration of the SOC(s) of interest in the feed and treated waters will be compared to the Manufacturer's statement of performance objectives for the equipment being tested. The ozone production and power usage may also be used to evaluate the performance of the equipment.

13.0 TASK 5: DATA MANAGEMENT

13.1 Introduction

The data management system used in the Verification Testing program shall involve the use of computer spreadsheet software and manual recording of the operational parameters for the water treatment equipment on a daily basis.

13.2 Experimental Objectives

The objectives of this task are: 1) to establish a viable structure for the recording and transmission of field testing data so the FTO will provide sufficient and reliable operational data for verification purposes, and 2) to provide the information needed for a statistical analysis of the data, as described in the "EPA/NSF ETV Protocol For Equipment Verification Testing For The Removal Of Synthetic Organic Chemical Contaminants: Requirements For All Studies."

13.3 Work Plan

The following protocol has been developed for data handling and data verification by the FTO. Where possible, a Supervisory Control and Data Acquisition (SCADA) system should be used for automatic entry of testing data into computer databases. Specific parcels of computer databases for operational and water quality parameters should then be downloaded by manual importation into Excel (or similar spreadsheet software) as a comma delimited file. These specific database parcels will be identified based upon discrete time spans and monitoring parameters. In spreadsheet form the data will be manipulated into a convenient framework to allow analysis of water treatment equipment operation. Backup of the computer databases to diskette should be performed on a monthly basis at a minimum. When SCADA systems are not available, direct instrument feed to data loggers and laptop computers shall be used when appropriate.

For parameters for which electronic data acquisition is not possible, field testing operators will record data and calculations by hand in laboratory notebooks (daily measurements will be recorded on specially-prepared data log sheets as appropriate). Each notebook must be permanently bound with consecutively numbered pages. Each notebook must indicate the starting and ending dates that apply to entries in the logbook. All pages will have appropriate headings to avoid entry omissions. All logbook entries must be made in black water insoluble ink. All corrections in any notebook shall be made by placing one line through the erroneous information. Products such as "correction fluids" are never to be utilized for making corrections to notebook entries. Operating logs shall include a description of the water treatment equipment (description of test runs, names of visitors, description of any problems or issues, etc.); such descriptions shall be provided in addition to experimental calculations and other items. The original notebooks will be stored on-site; photocopies will be forwarded to the project engineer of the FTO at an agreed upon schedule. This protocol will not only ease referencing the original data, but will also offer protection of the original record of results.

The database for the project will be set up in custom-designed spreadsheets. The spreadsheets will be capable of storing and manipulating each of the monitored water quality and operational parameters from each task, each sampling location, and each sampling time. All data from the laboratory notebooks and data log sheets will be entered into the appropriate spreadsheets. Data entry will be conducted on-site by the designated field testing operators. All recorded calculations will also be checked at this time. Following data entry, the spreadsheet will be printed out and the print-out will be checked against the handwritten data sheet. Any corrections will be noted on the hard-copies and corrected on the screen, and then a corrected version of the spreadsheet will be printed out. Each step of the verification process will be initialed by the field testing operator or engineer performing the entry or verification step.

Each experiment (e.g. verification run) will be assigned a run number that will then be tied to the data from that experiment through each step of data entry and analysis. As samples are collected and sent to state-certified or third party- or EPA-accredited laboratories, the data will be tracked by use of the same system of run numbers. Data from the outside laboratories will be received and reviewed by the field testing operator. These data will be entered into the data spreadsheets, corrected, and verified in the same manner as the field data.

13.4 Statistical Analysis

Water quality developed from grab samples collected during test runs according to the Analytical Schedule in Task 2 of this Test Plan shall be analyzed for statistical uncertainty. The FTO shall calculate 95% confidence intervals for grab sample data obtained during Verification Testing as described in "EPA/NSF ETV Protocol For Equipment Verification Testing For The Removal Of Synthetic Organic Chemical Contaminants: Requirements For All Studies." Statistical analysis could be carried out for a large variety of testing conditions.

The statistics developed will be helpful in demonstrating the degree of reliability with which water treatment equipment can attain quality goals. Information on the differences in feed water quality variations for entire test runs versus the quality produced during the optimized portions of the runs would be useful in evaluating appropriate operating procedures.

14.0 TASK 6: QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

14.1 Introduction

Quality assurance and quality control of the operation of the water treatment equipment and the measured water quality parameters shall be maintained during the Verification Testing program.

14.2 Experimental Objectives

The objective of this task is to maintain strict QA/QC methods and procedures during the ETV Program. Maintenance of strict QA/QC procedures is important in that if a question arises when analyzing or interpreting data collected for a given experiment, this information will be possible to verify exact conditions at the time of testing.

14.3 Work Plan

Equipment flow rates and associated signals should be verified and verification recorded on a routine basis. Daily routine walk-throughs during the testing program will be used to verify that each piece of equipment or instrumentation is operating properly. Particular care shall be taken to verify that chemicals are being fed at the defined flow rate, and into a flow stream that is operating at the expected flow rate. In addition, the operation of the air preparation equipment or the liquid oxygen supply for the ozone generator, and the ozone generator, shall be checked in each walkthrough and relevant operating data shall be recorded and checked to verify that operating conditions are within the acceptable operating range for the equipment or processes involved. In-line monitoring equipment such as flow meters, etc. will be checked as indicated below to verify that the readout matches with the actual measurement (i.e., flow rate) and that the signal being recorded is correct. The items listed are in addition to any specified checks outlined in the analytical methods.

When collecting water quantity data, all system flow meters will be calibrated using the classic bucket and stopwatch method where appropriate. Hydraulic data collection will include the measurement of the finished water flow rate by the “bucket test” method. This would consist of filling a calibrated vessel to a known volume and measuring the time to fill the vessel with a stopwatch. This will allow for a direct check of the system flow measuring devices.

14.3.1 Daily QA/QC Verifications

- On-line turbidimeter: Clean out reservoirs and recalibrate, check the flow rate (verified volumetrically over a specific time period).
- On-line pH meters (standardize and recalibrate).
- Chemical feed pump flow rates (check and verify components).
- On-line turbidimeter readings checked against a properly calibrated bench model.

14.3.2 QA/QC Verifications Performed Every Two Weeks

- On-line flow meters/rotameters: Clean equipment to remove any debris or biological buildup and verify flow volumetrically to avoid erroneous readings.
- Chemical feed pump flow rates (verify volumetrically over a specific period of time).

14.3.3 QA/QC Verifications Performed Every Testing Period

- Tubing: Verify that all tubing and connections are in good condition and replace if necessary. For surface water systems, microbial growth could occur between seasonal verification test runs, so replacement of tubing prior to each verification test may be necessary.
- Differential pressure transmitters (verify gauge readings and electrical signals using a pressure meter).

14.4 On-Site Analytical Methods

The analytical method utilized in this study for on-site monitoring of raw water and treated water quality are described in the following section. Use of either bench-top or in-line field analytical equipment will be acceptable for the verification testing; however, in-line equipment is recommended for ease of operation.

14.4.1 pH

Analysis for pH shall be performed according to Standard Method 4500-H⁺ B or EPA Method 150.1/150.2. A three-point calibration of any pH meter used in this study will be performed once per day when the instrument is in use. Certified pH buffers in the expected range shall be used. The pH probe shall be stored in the appropriate solution defined in the instrument manual. Transport of carbon dioxide across the air-water interface can confound pH measurement in poorly buffered waters. If this is a problem, measurement of pH in a confined vessel is recommended to minimize the effects of carbon dioxide loss with the atmosphere.

14.4.2 Turbidity Analysis

Turbidity analyses shall be performed according to Standard Method 2130 or EPA Method 180.1 with either a bench-top or in-line turbidimeter. Grab samples shall be analyzed using a bench-top turbidimeter; readings from this instrument will serve as reference measurements throughout the study. The bench-top turbidimeter shall be calibrated within the expected range of sample measurements at the beginning of Verification Testing and on a weekly basis using primary turbidity standards of 0.1, 0.5 and 3.0 NTU. Secondary turbidity standards shall be used on a daily basis to verify calibration of the turbidimeter and to recalibrate when more than one turbidity range is used.

During each verification testing period, the bench-top and in-line turbidimeters will be left on continuously. Once each turbidity measurement is complete, the unit will be switched back to its lowest setting. All glassware used for turbidity measurements will be cleaned and handled using lint-free tissues to prevent scratching. Sample vials will be stored inverted to prevent deposits from forming on the bottom surface of the cell.

The Field Testing Organization shall be required to document any problems experienced with the monitoring turbidity instruments, and shall also be required to document any subsequent modifications or enhancements made to monitoring instruments.

14.4.2.1 Bench-top Turbidimeters. The method for collecting grab samples will consist of running a slow, steady stream from the sample tap, triple-rinsing a dedicated sample beaker in this stream, allowing the sample to flow down the side of the beaker to minimize bubble entrainment, double-rinsing the sample vial with the sample, carefully pouring from the beaker down the side of the sample vial, wiping the sample vial clean, inserting the sample vial into the turbidimeter, and recording the measured turbidity.

When cold water samples cause the vial to fog and prevent accurate readings, allow the vial to warm up by submersing partially into a warm water bath for approximately 30 seconds.

14.4.2.2 In-line Turbidimeters. In-line turbidimeters may be used during verification testing and must be calibrated as specified in the manufacturer's operation and maintenance manual. It will be necessary to periodically verify the in-line readings using a bench-top turbidimeter; although the mechanism of analysis is not identical between the two instruments the readings should be comparable. Should these readings suggest inaccurate readings then all in-line turbidimeters should be recalibrated. In addition to calibration, periodic cleaning of the lens should be conducted using lint-free paper, to prevent any particle or microbiological build-up that could produce inaccurate readings. Periodic verification of the sample flow should also be performed using a volumetric measurement. Instrument bulbs should be replaced on an as-needed basis. It should also be verified that the LED readout matches the data recorded on the data acquisition system, if the latter is employed.

14.4.3 Dissolved Ozone

The dissolved ozone concentration can be measured using an indigo bleaching technique, such as Standard Method 4500-O₃ B or the HACH Indigo AccuVac method. When sampling for dissolved ozone, it is important to minimize sample agitation and transfer from one container to another. One good sampling technique is to collect the sample directly from the sample tap. If HACH AccuVac vials are used, the tip of the AccuVac can be placed directly into the tap opening where the water is flowing. Apply pressure and snap the tip while it is inside the sample tap opening. The vacuum in the AccuVac vial will draw the water sample into the AccuVac. Once the AccuVac is filled, remove the AccuVac from the sample tap and analyze according to the HACH instructions. If necessary, a short piece (i.e., less than 2 feet) of Tygon tubing can be attached to the sample tap for dissolved ozone sampling. If HACH AccuVac vials are not used, use of tubing attached to the sample port for sample collection is recommended to minimize sample agitation and mixing. This tubing should be Tygon and should be no longer than 2 feet in length.

Another method for measuring dissolved ozone is a dissolved ozone probe. These probes can be placed in the process stream to provide continuous measurements of ozone residuals. Check the probe tip daily to ensure that the membrane has been installed properly and that there are no air bubbles underneath the membrane. Also, check that the pressure and flow rate within the contactor are within the appropriate range for the probe being used. The performance of the probe shall be verified on a daily basis by measuring the dissolved ozone concentration with one of the indigo bleaching methods to ensure that the probe is functioning properly.

A third method for measuring dissolved ozone concentrations is an on-line analyzer which uses UV spectrophotometry to measure the gas-phase concentration of ozone which has been stripped from a liquid sample. These analyzers then correlate the gas-phase ozone concentration to the dissolved ozone concentration. These analyzers are calibrated at the factory.

14.4.4 Gas Phase Ozone

Gas phase ozone concentrations can be measured using either UV absorbance ozone monitors or a wet-chemistry test. Ozone monitors are calibrated at the factory and provide a continuous measure of the ozone concentration in gas phase. The wet-chemistry test method of measuring the ozone concentration of a gas stream involves bubbling ozone through a potassium iodide solution, acidification with sulfuric acid, and titration with sodium thiosulfate. This method is described in detail in Gordon *et al.* (1992). During each Verification Test, a wet-chemistry measurement of the ozone feed gas shall be conducted to independently check that the ozone monitor is functioning properly. If ozone monitors are not available, wet-chemistry tests shall be performed three times per day or three times per shift to measure the ozone concentration in the feed gas and off gas.

14.4.5 Hydrogen Peroxide

The concentration of hydrogen peroxide can be measured using one of two spectrophotometric methods: 1) cobalt-bicarbonate and 2) peroxidase. The cobalt-bicarbonate method, described in Masschelein *et al.* (1977), can be used to measure up to 2 mg/L hydrogen peroxide at 260 nm, whereas the peroxidase method, described in Bader *et al.* (1988), can be used to measure up to 1.7 mg/L hydrogen peroxide at 551 nm.

At low pH, ozone and peroxide can be in solution at the same time, because the reaction rate is slow. The presence of ozone interferes with any hydrogen peroxide analysis; therefore, to measure the amount of hydrogen peroxide in the AOP system, ozone production shall be temporarily terminated while hydrogen peroxide samples are being collected and analyzed.

To ensure the proper feed rate of hydrogen peroxide to the ozone/AOP system, use a stopwatch to measure the time required to collect a specified volume of hydrogen peroxide stock solution from the feed system. This requires that the hydrogen peroxide feed line to the contactor be temporarily disconnected so that the pumping rate of the stock hydrogen peroxide solution can be measured. Typically, a graduated cylinder is used to collect the pumped hydrogen peroxide sample and the size of the graduated cylinder is such that the length of collection time exceeds 10 seconds.

The strength of the peroxide feed solution can also be determined from the peroxide supplier's shipping information, as long as the peroxide being used for testing has not been: 1) diluted by the user; 2) exposed to contamination (which would affect its strength); 3) stored for longer than one year; or, 4) stored at temperatures greater than 77°F.

14.4.6 Temperature

Readings for temperature shall be conducted in accordance with *Standard Method 2550*. Raw water temperatures shall be obtained at least once daily. The thermometer shall have a scale marked for every 0.1 °C, as a minimum, and should be calibrated weekly against a precision thermometer certified by the National Institute of Standards and Technology (NIST). (A thermometer having a range of -1°C to +51°C, subdivided in 0.1° increments, would be appropriate for this work.)

14.4.7 Color

True color shall be measured with a spectrophotometer at 455 nm, using an adaptation of the *Standard Methods 2120* procedure. Samples shall be collected in clean plastic or glass bottles and analyzed as soon after collection as possible. If samples can not be analyzed immediately they shall be stored at 4°C for up to 24 hours, and then warmed to room temperature before analysis. The filtration system described in *Standard Methods 2120 C* shall be used, and results should be expressed in terms of PtCo color units.

14.4.8 Dissolved Oxygen

Analysis for dissolved oxygen shall be performed according to *Standard Method 4500-O* using an iodometric method or the membrane electrode method. The techniques described for sample collection must be followed very carefully to avoid causing changes in dissolved oxygen during the sampling event. Sampling for dissolved oxygen does not need to be coordinated with sampling for other water quality parameters, so dissolved oxygen samples should be taken at times when immediate analysis is going to be possible. This will eliminate problems that may be associated with holding samples for a period of time before the determination is made.

If the sampling probe is not mounted such that the probe is continuously exposed to the process stream, then care must be taken when measuring the dissolved oxygen concentration. For best results, collect the dissolved oxygen sample with minimal agitation and measure the dissolved oxygen concentration immediately. If possible, measure the dissolved oxygen under a continuous stream of sample by placing the tip of the probe in the sample container, allowing the sample to overflow the container while the probe reaches equilibrium (usually less than 5 minutes).

14.5 Chemical and Biological Samples Shipped Off-Site for Analysis

The analytical methods that shall be used during testing for chemical and biological samples that are shipped off-site for analyses are described in the section below.

14.5.1 Organic Samples

Samples for analysis of total organic carbon (TOC), UV₂₅₄ absorbance, and dissolved organic carbon (DOC) shall be collected in glass bottles supplied by the state-certified or third party- or EPA-accredited laboratory and shipped at 4 °C to the analytical laboratory within 24 hours of sampling. These samples shall be preserved in accordance with Standard Method 5010 B. Storage time before analysis shall be minimized, according to Standard Methods.

14.5.2 Algae

Algae samples shall be preserved with Lugol's solution after collection, stored and shipped in a cooler at a temperature of approximately 2 to 8 °C, and held at that temperature range until counted.

14.5.3 Inorganic Samples

Inorganic chemical samples, including alkalinity, shall be collected and preserved in accordance with Standard Method 2320 B. The samples shall be refrigerated at approximately 2 to 8 °C. Samples shall be processed for analysis by a state-certified or third party- or EPA-accredited laboratory within 24 hours of collection. The laboratory shall keep the samples at approximately 2 to 8 °C until initiation of analysis.

Bromate samples shall be collected in sampling containers supplied by the state-certified or third party- or EPA-accredited laboratory. Sample collection and storage requirements are outlined in EPA Method 300.1 or shall be provided by the laboratory conducting the analysis.

14.5.4 SOC Analysis

Analysis of SOC's requires a trained analyst using sophisticated instrumentation. Only state-certified or third party- or EPA-accredited laboratories shall analyze SOC samples that are collected during Initial Operations and Verification Testing. As stated in the "EPA/NSF ETV Protocol For Equipment Verification Testing For The Removal Of Synthetic Organic Chemical Contaminants: Requirements For All Studies," approved methods for some SOC's may not be available, and for these SOC's, a proposed, peer-reviewed method may be used.

There are many approved methods for analyzing Phase II and Phase V SOC's. Depending on the laboratory, gas chromatography (GC) or high performance liquid chromatography (HPLC) methods can be used to analyze SOC's. For both methods, the equipment is highly specialized and proper operation of these instruments requires a skilled laboratory technician.

Mass spectrometry is not required for all SOC's, however it is recommended for SOC identification. Retention times relative to the internal standard can also be used to identify SOC's. Either peak height or peak area can be used to determine the SOC concentrations.

SOC's shall be analyzed with an internal standard similar in analytical behavior and not affected by the matrix for QA/QC. An appropriate surrogate standard shall also be used during SOC analysis. Data pertaining to the internal and surrogate standards shall be reported with the SOC concentrations of the samples being analyzed. A method blank shall also be prepared and analyzed by the state-certified or third party- or EPA-accredited laboratory to verify minimal contamination in the laboratory.

At least three standards shall be used to develop the standard curve for SOC quantification and these three standards shall be extracted and analyzed (by GC or HPLC) on the same day as the samples.

During each Verification Test period, one treated water sample shall be analyzed by scanning for the presence and concentration of potential by-products of SOC oxidation by ozone. Gas chromatography followed by mass spectrometry can be used to identify many of the organic by-products formed by ozonation. The spectra obtained by this analysis can be matched to a compound library in a computer database to identify the various byproducts. This analysis shall be performed by a state-certified or third party- or EPA-accredited analytical laboratory. The scan should be targeted toward the SOC of interest, and the potential by-products associated with ozonation of that SOC.

Spiked samples shall be analyzed once, at the beginning of each Verification Test Run. The laboratory shall spike a feed water sample with a known quantity of the SOC(s) of interest and

analyze this spiked sample. SOC analysis of the spiked sample will indicate if there are any interferences present in the feed water. The broad scan can be a performance-based scan (i.e., the scan is not used for compliance, and therefore undergoes less rigorous QA/QC and is less expensive than a compliance based scan analysis.)

14.6 Experimental QA/QC Samples

14.6.1 Process Control

A second round of testing shall be carried out using procedures identical to the steps outlined above, but without operating the ozone or ozone/AOP equipment. The purpose of this testing is to evaluate any cumulative effects produced by the equipment, the spiking and sampling procedures, and the sample handling procedures on SOC(s). The process control samples should show minimal loss of SOC(s) relative to the trip control sample. Significant loss of SOC concentrations in the process control sample indicates that some aspect of the process other than ozone oxidation contributes to SOC removal. Re-testing is required when this is shown to occur.

14.6.2 Trip Control

For tests utilizing spiked SOC(s), a replicate or subsample of the spiking solution shall accompany the actual spiking solution from the analytical laboratory. This replicate sample shall undergo all of the processes used on the actual solution including dose preparation, shipping, preparation for spiking, and return to the laboratory for analysis. The trip control samples should show minimal loss of SOC(s). Significant decreases in the SOC concentration of the trip control sample indicates that some step in handling the solution contributed to the reduction in the SOC concentration. The seeding tests must be repeated when significant loss of SOC(s) in the trip control sample is observed.

15.0 OPERATION AND MAINTENANCE

The FTO shall obtain the Manufacturer-supplied Operation and Maintenance (O&M) Manual to evaluate the instructions and procedures for their applicability during the verification testing period. The following are recommendations for criteria for O&M Manuals for drinking water treatment equipment employing ozone treatment.

15.1 Maintenance

The Manufacturer shall provide readily understood information on the recommended or required maintenance schedule for each piece of operating equipment including, but not limited to, the following, where applicable:

- ozone generator (dielectric replacement)

- ozone diffusers or injection port, control valves
- ozone destruct unit (catalyst replacement)
- gas phase ozone monitors (for feed gas and off gas)
- dissolved ozone monitoring equipment
- cooling water equipment
- air preparation unit or oxygen feed system for ozone generation
- gas and liquid rotameters
- UV lamps and other relevant equipment
- peroxide feed equipment
- other equipment such as pumps and valves

The Manufacturer shall also provide readily understood information on the recommended or required maintenance for non-mechanical or non-electrical equipment, including but not limited to, the following, where applicable:

- piping
- contactor chamber

15.2 Operation

The Manufacturer shall provide readily understood recommendations for procedures related to proper operation of all equipment. Among the operating aspects that should be addressed in the O&M manual are:

Ozone Generator

- air preparation or oxygen feed requirements (moisture content, filtration requirements, flow rate)
- cooling water requirements (flow)
- range of variable voltage for adjusting ozone output
- proper sequence of operation for start-up and shut-down
- proper sequence of operation for initial start-up or for re-start after maintenance

Ozone Monitors (Gas Phase)

- temperature and pressure compensation
- zeroing and calibration procedures
- proper sequence of operation for start-up and shut-down

Ozone Destruct Units

- heater and/or blower requirements
- catalyst requirements
- proper sequence of operation for start-up and shut-down

Air Preparation or Oxygen Feed Systems

- desiccant requirements and replacement procedures
- filters (maintenance and replacement schedule)
- proper sequence of operation for start-up and shut-down

- supplemental gas (air or nitrogen) flow rate, pressure, and temperature.

Cooling Water System

- maintenance of proper temperature
- monitoring cooling water flow
- pump maintenance
- proper sequence of operation for start-up and shut-down
- maintenance of recirculation equipment, if cooling water is recirculated

Ozone Contactor Systems

- maintenance schedule and procedures
- replacement procedures

UV lamps

- hours of operation (verification procedures)
- UV irradiance (calibration and verification procedures)
- maintenance schedule and procedures
- replacement procedures
- proper sequence of operation for start-up and shut-down

Hydrogen Peroxide Feed System

- procedures for variable speed adjustments to pump
- information about proper tubing type and size
- anticipated schedule for tubing replacement
- storage information (i.e., safety, container type, container material, temperature, length of storage time) for stock hydrogen peroxide solutions
- proper sequence of operation for start-up and shut-down

Control Valves

- open/close indication
- sequence of operations

The Manufacturer shall provide a troubleshooting guide; a simple checklist of what to do for a variety of problems, including but not limited to:

- no flow to unit
- sudden change in flow to unit
- no electric power
- automatic operation (if provided) not functioning
- valve stuck or will not operate

16.0 REFERENCES

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Table 1. Water Quality Sampling and Measurement Schedule

Parameter	Sampling Location	Mandatory (M) or Optional (O)	Frequency*	
			Surface Water Systems	Groundwater Systems
Temperature (°C)	Feed Water, Treated water	M	3/d or 3/shift	3/d or 3/shift
Dissolved Ozone Residual (mg/L)	Treated†	O	3/d or 3/shift	3/d or 3/shift
pH	Feed Water	M	3/d or 3/shift	3/d or 3/shift
Total Alkalinity (mg/L as CaCO ₃)	Feed Water	O	1/d	1/d
Total Organic Carbon (mg/L)	Feed Water	O	1/25 hours of ozone production	1/50 hours of ozone production
Dissolved Organic Carbon (mg/L)	Feed Water	O	1/25 hours of ozone production	1/50 hours of ozone production
UV absorbance at 254 nm (1/m)	Feed Water, Treated water	O	1/d	1/50 hours of ozone production
Color (Pt-Co)	Feed Water, Treated water	O	1/d	1/50 hours of ozone production
Turbidity (NTU)	Feed Water, treated water	O	3/d or 3/shift	1/d
Bromide (mg/L)	Feed Water	O	1/50 hours of ozone production	1/50 hours of ozone production

Table 1. Water Quality Sampling and Measurement Schedule (continued)

Parameter	Sampling Location	Mandatory (M) or Optional (O)	Frequency*	
			Surface Water Systems	Groundwater Systems
Bromate (µg/L)	Treated Water	O	1/50 hours of ozone production	1/50 hours of ozone production
SOCs (µg/L)	Feed Water, Treated water	M	1 per 25 hours of ozone production	1 per 25 hours of ozone production
SOC scan	Feed Water, Treated water	M	1 per Verification test period, after 100 th hour of operation	1 per Verification test period, after 100 th hour of operation
Total THM (µg/L) (chloroform, bromoform, bromodichloromethane, dibromochloromethane)	Treated Water	O	1/50 hours of ozone production	1/50 hours of ozone production
HAA ₅ (µg/L) (monochloroacetic acid, monobromoacetic acid, dichloroacetic acid, dibromoacetic acid, trichloroacetic acid)	Treated Water	O	1/50 hours of ozone production	1/50 hours of ozone production
Iron (µg/L)	Feed Water	O	1/50 hours of ozone production	1/50 hours of ozone production
Dissolved Manganese (µg/L) (Manganese concentration passing through 0.2 µm filter)	Feed Water, Treated water	O	1/50 hours of ozone production	1/50 hours of ozone production
Total Manganese (µg/L)	Feed Water, Treated water	O	1/50 hours of ozone production	1/50 hours of ozone production

Table 1. Water Quality Sampling and Measurement Schedule (continued)

Parameter	Sampling Location	Mandatory (M) or Optional (O)	Frequency*	
			Surface Water Systems	Groundwater Systems
Total Sulfides	Feed Water	O	1/d	1/d
Dissolved Oxygen	Feed Water, Treated water	O	1/50 hours of ozone production	1/50 hours of ozone production
Hydrogen Peroxide (mg/L)	Stock Solution, Treated Water	M††	1/50 hours of ozone production 1/Verification Test Period	1/50 hours of ozone production 1/Verification Test Period
Quenching Solution (mg/L) (e.g., hydrogen peroxide)	Feed Water	M	1/d	1/d
Algal enumeration and species	Feed Water	O	1 per Verification Test Period	Not Required
Calcium (mg/L as CaCO ₃)	Feed Water	O	1/50 hours of ozone production	1/50 hours of ozone production
Total Hardness (mg/L as CaCO ₃)	Feed Water	O	1/50 hours of ozone production	1/50 hours of ozone production

* 3/d or 3/shift means that the water quality parameter shall be measured either 3 times per day if ozone production is continuous over the 200 hours of Verification Testing, or 3 times per staffed shift if ozone production is periodically terminated or interrupted, and the length of time of ozone production is less than 24 hours. 1/50 hours of ozone production means that the water quality parameter shall be measured once per each 50 hours of ozone production, regardless of interruptions in ozone production. † The dissolved ozone concentration should be measured at sampling ports within the ozone contactor or immediately at the outlet of the ozone contactor. If the ozone decay coefficient is being determined, at least two sampling ports will need to be sampled. †† The peroxide concentration of the stock solution shall be checked at the prescribed frequency. The peroxide concentration within the contactor shall be checked once during or immediately prior to the verification testing period, while the ozone equipment is not operating. Peroxide monitoring within the contactor will require that samples be withdrawn at appropriate sampling ports at the end or outlet of the contactor.

Table 2. Analytical Methods

Parameter	Facility	Standard Methods number or Alternative Reference¹	EPA Method²
Temperature (°C)	On-site	2550 B	
Dissolved Ozone Residual (mg/L)	On-site	4500 O ₃ B; HACH Indigo Blue Method*	
pH	On-site	4500 H ⁺	150.1/150.2
Total Alkalinity (mg/L as CaCO ₃)	Lab	2320 B	
Phase II and Phase V SOCs	Lab	6252, 6410, 6420, 6431, 6440, 6610, 6630, 6640, 6651	525.2, 505, 515.1, 531.1, 547, 548.1, 549.1, 1613
Total Organic Carbon (mg/L)	Lab	5310 C	
Dissolved Organic Carbon (mg/L)	Lab	5310 C	
UV absorbance at 254 nm (1/m)	Lab	5910 B	
Color (Pt-Co)	Lab	2120 C	110.2
Turbidity (NTU)	On-site	2130 B	180.1
Bromide (mg/L)	Lab	4500-Br ⁻	300.0
Bromate (µg/L)	Lab		300.1
Total THM (µg/L)	Lab	6232 B	502.2, 524.2, 551
HAA ₅ (µg/L)	Lab	6251 B	552.1
Iron (µg/L)	Lab	3111 B, 3113 B, 3120 B	200.7, 200.8, 200.9
Total Manganese (µg/L)	Lab	3111 B, 3113 B, 3120 B	200.7, 200.8, 200.9
Dissolved Manganese (µg/L) (Manganese concentration passing through 0.2 µm filter)	Lab	3500-Mn	3111 B, 3113 B, 3120 B
Total Sulfides	Lab or On-Site	4500-S ²⁻ D, E	
Dissolved Oxygen	Lab or On-Site	4500-O	

Table 2. Analytical Methods (continued)

Parameter	Facility	<i>Standard Methods</i> number or Alternative Reference¹	EPA Method²
Algal enumeration and speciation	Lab	Part 10000, Biological Examination†	
Parameter	Facility	<i>Standard Methods</i> number or Alternative Reference ¹	EPA Method ²
Calcium (mg/L as CaCO ₃)	Lab	3500-Ca D, 3111 B, 3120 B	200.7
Total Hardness (mg/L as CaCO ₃)	Lab	2340 C	
SOC scan	Lab	6410B, 6420C, 6440C	525.2 – Extended for Broad Spectrum

¹ Standard Method Source: 20th Edition of Standard Methods for the Examination of Water and Wastewater, 1999, American Water Works Association.

² EPA Methods Source: EPA Office of Ground Water and Drinking Water. EPA Methods are available from the National Technical Information Service (NTIS).

* Dissolved ozone residual measurements can also be from a properly calibrated and installed dissolved ozone monitor or properly calibrated and installed dissolved ozone monitor.

† *Standard Methods* does not contain a method for enumeration and speciation of algae. It does, however, contain methods for laboratory techniques that may need to be performed for proper enumeration and speciation of the algae. Only an experienced and qualified laboratory analyst shall conduct algal enumeration and speciation.

Table 3. System Operating Data

Operational Parameter		Frequency
Water Flow (gpm)	Feed Water	3/d or 3/shift
	Side Stream (if applicable)	3/d or 3/shift
	Cooling Water	3/d or 3/shift
Water Pressure (psig)	Inlet to Ozone System	3/d or 3/shift
	Outlet of Ozone System	3/d or 3/shift
	Side Stream (if applicable)	3/d or 3/shift
	Cooling Water	3/d or 3/shift
Water Temperature (°C)	Inlet to Ozone System	3/d or 3/shift
	Outlet of Ozone System	3/d or 3/shift
	Side Stream (if applicable)	3/d or 3/shift
Gas Phase Ozone Concentration (% wt)	Feed Gas	3/d or 3/shift
	Off Gas	3/d or 3/shift
Power Usage (kw/hr)	Ozone Generator	3/d or 3/shift
	Air Preparation System or Oxygen System	3/d or 3/shift
	Gas Phase Ozone Feed and Off Gas Monitors	3/d or 3/shift
	Cooling Water System	3/d or 3/shift
	Destruct Units	3/d or 3/shift
	Other pumps or motors	3/d or 3/shift
Ozone Feed Gas Temperature (°C)		3/d or 3/shift
Ozone Feed Gas Pressure (psig)		3/d or 3/shift
Ozone Feed Gas Flow (scfm)		3/d or 3/shift
Atmospheric Pressure (psia)		1/d
Dew Point (if using air feed system)		1/d
Ozone Production (lb/d)		1/d
Ozone Decay Rate (1/minute) (optional)		1/d
If applicable: Peroxide feed concentration (mg/L) Peroxide feed rate (mL/min) Peroxide to Ozone ratio (by weight)		3/d or 3/shift
If applicable: Purity of oxygen supply (%) Supplemental nitrogen flow rate (scfm), pressure (psig), and temperature (°C) Supplemental air flow rate (scfm), pressure (psig), and temperature (°C)		1/d or 1/shift 1/d or 1/shift 1/d or 1/shift
If applicable: Operating parameters for UV-light systems (see ETV Equipment Verification Testing Plan for Microorganism Contaminant Inactivation by Ultraviolet Based Technology)		3/d or 3/shift